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Synthesis, Structure, and Binding Property of Pentiptycene-Based Rigid Tweezer-like Molecules

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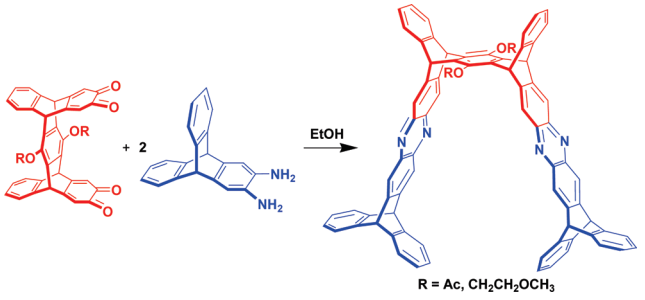

A series of pentiptycene-derived rigid tweezer-like molecules have been efficiently synthesized, and their structures have been determined by NMR, MS spectra, and X-ray analysis. Moreover, it was also found that molecular tweezer **15** showed efficient binding ability toward C_{60}.

The design and synthesis of novel receptors with the capability for selective and efficient substrate binding are of fundamental importance in host−guest chemistry.[1,2] Besides the frequently used well-preorganized cyclic receptors, the noncyclic receptors with cavities of flexible size, which were usually called molecular tweezers and clips, also proved to be effective.[2,3] Recently, the well-preorganized molecular tweezers,[4] especially the rigid ones,[5] which are composed of two aromatic groups positioned by a relatively rigid tether, have attracted increasing interest.

Pentiptycene,[6] with its unique rigid, aromatic, and H-shaped scaffold, has found specific applications in porous materials,[7a,b] low dielectric constant materials,[7c] materials with monolayer assembly structures,[7d−f] molecular machines,[7g] and fluorescent chemosensors.[7h,i] Recently, we synthesized several pentiptycene-derived crown ethers, and found that they could show highly efficient complexation abilities toward paraquat derivatives and cyclobis(paraquat-*p*-phenylene).[8] Furthermore, we envisioned that proper pentiptycene derivatives could also be utilized as useful building blocks for developing novel rigid receptors with concave−convex topology, which could subsequently find wide potential applications in host−guest chemistry. Herein, we report the efficient synthesis of a series of pentiptycene-derived rigid tweezer-like molecules by the condensation of pentiptycene-based *o*-quinones **1**−**6** (Figure 1) with proper *o*-diamino-substituted compounds. Moreover, we also found that the molecular tweezer **15** with the suitable size showed efficient binding property with C_{60}.

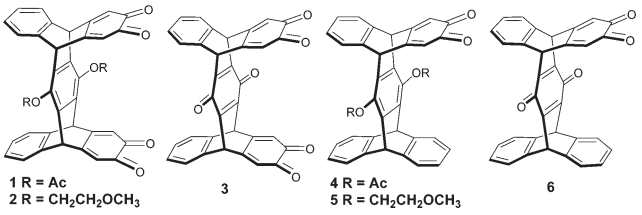

FIGURE 1. Structures of pentiptycene-based *o*-quinones **1**−**6**.

The pentiptycene derivatives **1**−**6** were prepared according to the method described previously.[8] As shown in Scheme 1, compounds **9**−**14** could be conveniently and efficiently synthesized in reasonable yields by condensation of *o*-diaminobenzene **7** with the corresponding *o*-quinones **1**−**6** in refluxing ethanol for 3−6 h.[9] In the ^{1}H NMR spectra, it was found that compounds **9**−**11** all showed one singlet for the bridgehead

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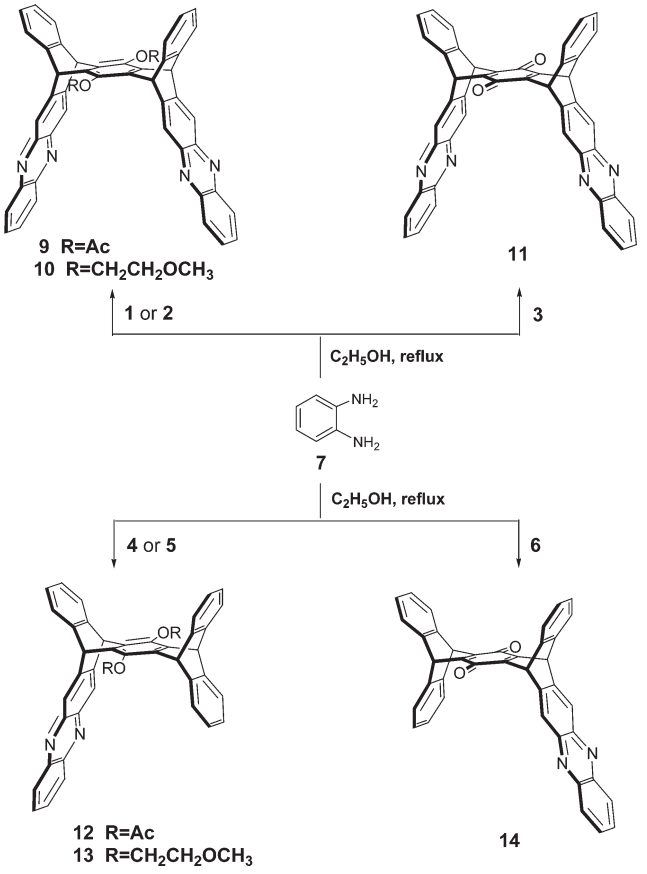
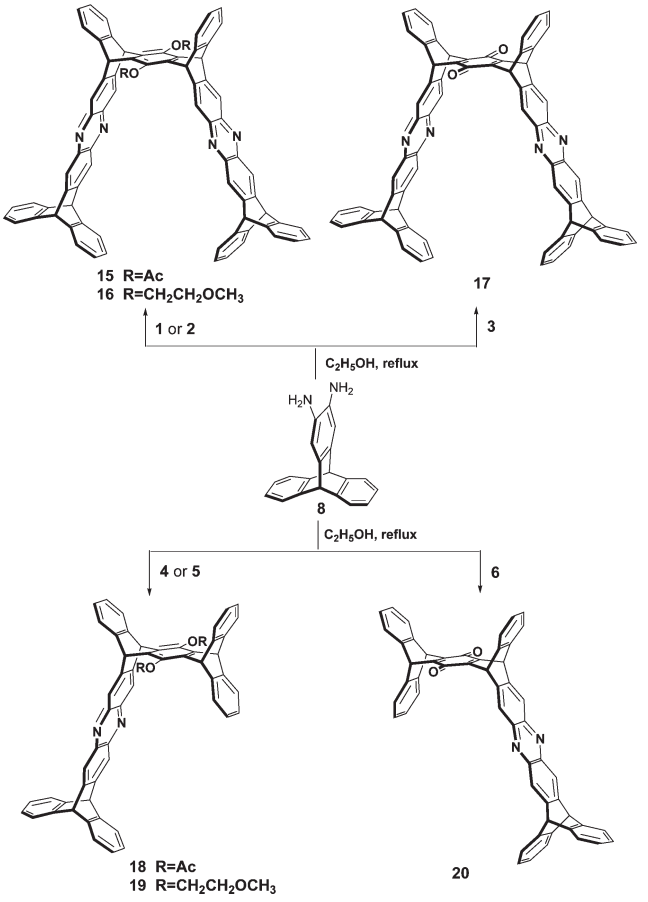
SCHEME 1. Synthesis of Tweezer-like Molecules 9−14



SCHEME 2. Synthesis of Tweezer-like Molecules 15−20



(methenyl) protons, while **12**−**14** showed two singlets for the bridgehead protons.[10] These observations suggested that **9**−**11** had C_{2v} symmetric structures, while compounds **12**−**14** had C_s symmetric structures.

Similarly, the tweezer-like molecules **15**−**20** also could be synthesized expediently in 58−64% yields by the reaction of *o*-quinones **1**−**6** and *o*-diaminotriptycene **8**[9a] in refluxing ethanol overnight (Scheme 2). In the ^{1}H NMR spectra of **15**−**17**, two singlets for bridgehead protons (one for the pentiptycene moiety, the other for the triptycene moieties) and two singlets for the CH=CH protons of the phenazine rings were observed, which suggested their highly symmetric structures of C_{2v}. For **18**−**20**, their ^{1}H NMR spectra showed three singlets for the bridgehead protons (two singlets for the pentiptycene moiety, the third one for the triptycene moiety), and two singlets for the CH=CH protons of the phenazine rings, which are consistent with their C_s symmetric structures.

It was found that the chemical shifts of the bridgehead protons in the tweezer-like molecules are dependent on not only the substituents in the central ring of the pentiptycene moiety, but also the number of substituted aromatic rings adjacent to the bridgehead. Consequently, the bridgehead proton adjacent to the phenazine group in **12** showed downfield shift by ca. 0.2 ppm compared to the bridgehead proton without the adjacent phenazine group.[10] The bridgehead proton with an adjacent ether chain on the central ring of the pentipycene moiety in **13** showed downfield shift by ca. 0.04 ppm, while the bridgehead proton signal with an adjacent ester group in **12** shifted upfield by ca. 0.4 ppm, compared to the one with the quinone group on the central ring of the pentiptycene moiety in **14**. These trends have also been observed in the ^{1}H NMR spectra of tweezer-like molecules **18**−**20**.

We also obtained the X-ray single-crystal structure of compound **10**.[11] As shown in Figure 2, the tweezer-like molecule showed a little distortion in the pyrazine rings in the solid state. Two pyrazine rings of one molecule **10** positioned inside and outside the cavity of its adjacent molecule tweezers, and are parallel to the adjacent pyrazine rings with a distance of 3.672 and 3.846 Å, respectively. The alternate arrangement of the adjacent molecules resulted in a 1D superstructure, which can further self-assemble into a 2D-layered structure, and 3D open-framework, in which the multiple C−H···N hydrogen bonding[10] and $\pi-\pi$ stacking interactions between the adjacent molecules play an important role.

We also tested the complexation property of the tweezer-like molecule **15** with suitable size toward fullerene C_{60}.[10,12]

(10) See the Supporting Information for details.

(11) Crystal data for **10**: $C_{52}H_{38}N_4O_4$, M_w = 782.86, crystal size 0.50 × 0.32 × 0.15 mm^3, triclinic, space group $P\bar{1}$, a = 9.780(4) Å, b = 14.434(4) Å, c = 21.796(7) Å, α = 92.708(11)°, β = 86.307(12)°, γ = 87.862(13)°, U = 2931.1(17) Å^3, Z = 2, D_c = 0.887 Mg/m^3, T = 173(2) K, μ = 0.057 mm^{-1}, 30709 reflections measured, 10620 unique (R_{int} = 0.0458), final R indices [$I > 2\sigma(I)$]: R_1 = 0.0891, wR_2 = 0.2424, R indices (all data): R_1 = 0.1166, wR_2 = 0.2634.

(12) Although molecule **16** has almost the same cavity size as that of **15**, its poor solubility in toluene/$CHCl_3$ makes its interaction with C_{60} hard to observe. For molecule **17**, it also showed no binding affinity toward C_{60} probably due to its electron-deficient cavity. Similarly, we found that the electron-deficient and/or open pockets of molecules **9**−**14** and **17**−**20** also made them show no binding affinities toward C_{60}.

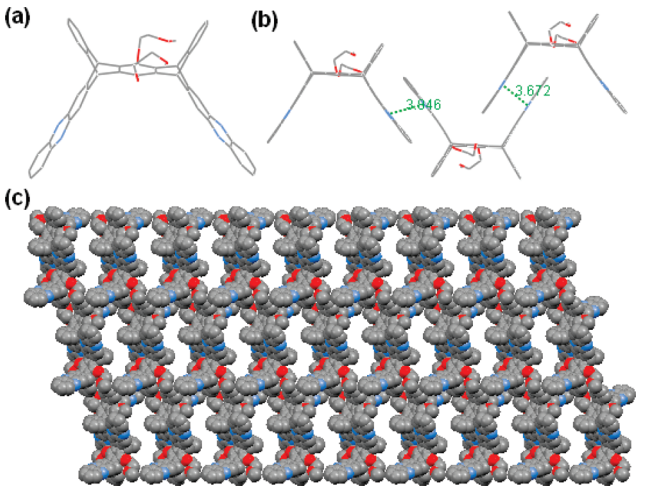


FIGURE 2. (a) View of the crystal structure of **10**. (b) View of the π stacked dimers. (c) A 3D assembly viewed along the *a*-axis. Solvent molecules and hydrogen atoms are omitted for clarity.

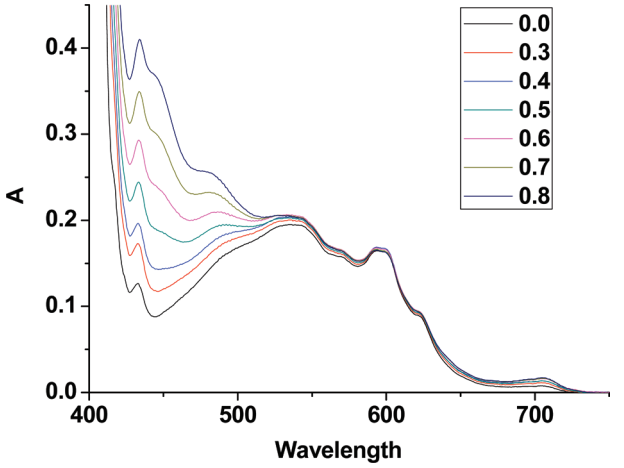


FIGURE 3. Absorption spectra of $\mathbf{C_{60}}$ (2.179×10^{-4} mol dm^{-3}) in the presence of **15** in $CHCl_3$/toluene (1:1) at 298 K. The concentrations of **15** for curves 1−7 (from bottom to top) are the following: 0.0, 0.653, 0.870, 1.088, 1.305, 1.523, 1.740 ($\times 10^{-4}$ mol dm^{-3}).

Consequently, when **15** (2.18×10^{-4} M) and 1 equiv of C_{60} were mixed in 1:1 toluene/chloroform, the solution gradually became yellow. This observation suggested the complexation between **15** and C_{60} occurred, and the $\pi-\pi$ interaction and the van der Waals force between sterically fitted concave and convex π surfaces of the pentiptycene, triptycene moieties, and C_{60} might play an important role.[13] The UV/vis spectroscopic experiments further afforded a quantitative estimate for the complexation between **15** and C_{60}. First, 1:1 complexation of **15** with C_{60} in toluene/chloroform (1:1, v/v) was obtained by the Job plot.[10,14] The UV/vis titrations showed that upon the addition of **15** to a solution of C_{60} in 1:1 toluene/chloroform, the absorption between 430 and 510 nm gradually increases (Figure 3). Accordingly, the apparent association constant K_a was calculated to be 3500 mol^{-1} L by the Benesi−Hildebrand equation.[10]

In summary, we have synthesized a series of pentiptycene-based rigid tweezer-like molecules containing one or two pyrazine groups, and found that tweezer-like molecule **10** could assemble into a 3D open-framework in the solid state. Moreover, molecular tweezer **15** with the suitable size showed efficient binding ability toward C_{60}. Design and synthesis of other pentiptycene-based rigid molecular receptors and their applications in supramolecular chemistry are underway in our laboratory.

Experimental Section

General Methods for Synthesis of Compounds 9−20. A mixture of the corresponding *o*-quinone (1 equiv) and 2,3-diaminotriptycene **7** or *o*-diaminobenzene **8** (1 equiv for a *o*-quinone moiety) in EtOH was refluxed under Ar overnight. The cooled solution was filtered. The filtrate was washed with CH_3OH, and then purified by column chromatography over silica gel (eluent: CH_2Cl_2/CH_3OH except CH_2Cl_2/ethyl acetate for **14** and **20**) to give the product as a yellow solid.

9: starting from **1** (100 mg, 0.16 mmol) and **7** (36 mg, 0.32 mmol). Yield: 61% (76 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (s, 6H), 5.58 (s, 4H), 7.06−7.09 (m, 4H), 7.42−7.45 (m, 4H), 7.67−7.70 (m, 4H), 7.97 (s, 4H), 8.06−8.09 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 48.3, 122.9, 124.4, 126.6, 129.3, 129.8, 135.3, 139.0, 142.1, 142.8, 142.9, 144.9, 168.4. MALDI-TOF MS: m/z 751.4 $[M + H]^+$. Anal. Calcd for $C_{50}H_{30}N_4O_4 \cdot H_2O$: C, 78.11; H, 4.20; N, 7.29. Found: C, 78.35; H, 4.51; N, 7.08.

10: starting from **2** (100 mg, 0.16 mmol) and **7** (36 mg, 0.32 mmol). Yield: 65% (80 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 6H), 3.96−3.99 (m, 4H), 4.14−4.17 (m, 4H), 6.09 (s, 4H), 7.04−7.07 (m, 4H), 7.45−7.48 (m, 4H), 7.69−7.73 (m, 4H), 8.06 (s, 4H), 8.09−8.13 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.5, 59.6, 71.9, 75.5, 122.3, 124.4, 126.3, 129.2, 129.8, 135.6, 142.8, 143.0, 146.7. MALDI-TOF MS: m/z 783.4 $[M + H]^+$. Anal. Calcd for $C_{52}H_{38}N_4O_4 \cdot 0.2H_2O$: C, 79.41; H, 4.92; N, 7.12. Found: C, 79.18; H, 4.96; N, 7.04.

11:[15] starting from **3** (120 mg, 0.23 mmol) and **7** (50 mg, 0.46 mmol). Yield: 70% (107 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.02 (s, 4H), 7.10−7.12 (m, 4H), 7.49−7.52 (m, 4H), 7.71−7.75 (m, 4H), 8.07 (s, 4H), 8.10−8.13 (m, 4H). MALDI-TOF MS: m/z 665.3 $[M + H]^+$. Anal. Calcd for $C_{46}H_{24}N_4O_2 \cdot 3.5CH_3OH$: C, 76.53; H, 4.93; N, 7.21. Found: C, 76.58; H, 4.28; N, 7.14. HRMS (FTICR) calcd for $C_{46}H_{25}N_4O_2$ $[M + H]^+$ 665.1972, found 665.1956; $C_{46}H_{27}N_4O_2$ $[M + 3H]^+$ 667.2128, found 667.2120.

12: starting from **4** (100 mg, 0.17 mmol) and **7** (19 mg, 0.17 mmol). Yield: 61% (67 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.68 (s, 6H), 5.34 (s, 2H), 5.55 (s, 2H), 6.86−6.89 (m, 2H), 6.93−6.96 (m, 2H), 7.04−7.07 (m, 2H), 7.24−7.26 (m, 2H), 7.28−7.31 (m, 2H), 7.39−7.42 (m, 2H), 7.72−7.76 (m, 2H), 8.00 (s, 2H), 8.13−8.17 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 48.2, 48.8, 122.6, 123.9, 124.4, 125.4, 125.5, 126.5, 129.2, 130.0, 134.1, 137.4, 138.8, 142.2, 144.0, 144.2, 168.5. MALDI-TOF MS: m/z 649.4 $[M + H]^+$, 671.4 $[M + Na]^+$, 687.3 $[M + K]^+$. Anal. Calcd for $C_{44}H_{28}N_2O_4 \cdot 2H_2O$: C, 77.18; H, 4.71; N, 4.09. Found: C, 77.32; H, 4.51; N, 4.15.

13: starting from **5** (100 mg, 0.16 mmol) and **7** (18 mg, 0.16 mmol).Yield: 80% (87 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 6H), 3.91−3.94 (m, 4H), 4.07−4.15 (m, 4H), 5.80 (s, 2H), 6.04 (s, 2H), 6.89−6.90 (m, 2H), 6.92−6.95 (m, 2H), 7.04−7.06 (m, 2H), 7.29−7.39 (m, 4H), 7.41−7.49 (m, 2H),

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(15) As it has poor solubility in even DMSO, we could not obtain its ^{13}C NMR spectrum.

7.71−7.79 (m, 2H), 8.06 (s, 2H), 8.12−8.21 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.5, 48.2, 59.5, 71.9, 75.2, 122.2, 123.6, 123.7, 124.3, 125.2, 126.2, 129.3, 129.8, 134.5, 137.6, 142.8, 143.3, 145.2, 145.3, 146.2. MALDI-TOF MS: *m*/*z* 682.5 $[M]^+$. Anal. Calcd for $C_{46}H_{38}N_2O_4 \cdot 0.5CH_2Cl_2$: C, 77.01; H, 5.42; N, 3.86. Found: C, 77.18; H, 5.09; N, 3.98. HRMS (FTICR) calcd for $C_{46}H_{37}N_2O_4$ $[M - 1]^+$ 681.2748, found 681.2755.

14: starting from **6** (80 mg, 0.16 mmol) and **7** (18 mg, 0.16 mmol). Yield: 64% (58 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (s, 2H), 5.99 (s, 2H), 6.92−6.94 (m, 2H), 6.97−7.00 (m, 2H), 7.08−7.11 (m, 2H), 7.35−7.40 (m, 4H), 7.46−7.49 (m, 2H), 7.79−7.82 (m, 2H), 8.13 (s, 2H), 8.21−8.24 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.6, 47.5, 123.5, 124.3, 124.8, 125.5, 125.6, 126.6, 129.4, 130.1, 141.7, 142.4, 143.1, 143.6, 144.1, 148.9, 151.4, 179.7. MALDI-TOF MS: *m*/*z* 564.3 $[M + 2H]^+$. Anal. Calcd for $C_{46}H_{24}N_4O_2 \cdot 1.8H_2O$: C, 82.18; H, 4.01; N, 4.36. Found: C, 82.19; H, 4.20; N, 4.18.

15: starting from **1** (51 mg, 0.10 mmol) and **8** (57 mg, 0.20 mmol). Yield: 58% (64 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.68 (s, 6H), 5.51 (s, 4H), 5.55 (s, 4H), 6.99−7.04 (m, 12H), 7.36−7.42 (m, 12H), 7.89 (s, 4H), 7.91 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6, 48.4, 122.2, 122.8, 123.9, 124.0, 124.3, 126.1, 126.4, 135.4, 139.0, 142.2, 142.3, 142.5, 143.3, 143.5, 144.2, 145.9, 168.3. MALDI-TOF MS: *m*/*z* 1103.5 $[M + H]^+$. Anal. Calcd for $C_{78}H_{46}N_4O_4 \cdot 3H_2O$: C, 80.95; H, 4.53; N, 4.84. Found: C, 81.24; H, 4.51; N, 4.75.

16: starting from **2** (200 mg, 0.31 mmol) and **8** (177 mg, 0.62 mmol). Yield: 60% (210 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.73 (s, 6H), 3.94−3.95 (m, 4H), 4.12−4.17 (m, 4H), 5.57 (s, 4H), 6.02 (s, 4H), 6.98−7.06 (m, 12H), 7.42−7.43 (m, 12H), 7.95 (s, 4H), 7.98 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.7, 47.6, 53.5, 59.5, 71.9, 75.4, 122.3, 124.1, 124.3, 126.1, 135.6, 142.2, 143.4, 143.5, 145.9, 146.4. MALDI-TOF MS: *m*/*z* 1135.3 $[M + H]^+$. Anal. Calcd for $C_{80}H_{54}N_4O_6 \cdot 2.5H_2O$: C, 81.40; H, 5.04; N, 4.75. Found: C, 81.54; H, 4.91; N, 4.68.

17: starting from **3** (150 mg, 0.29 mmol) and **8** (165 mg, 0.58 mmol). Yield: 62% (183 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 4H), 5.96 (s, 4H), 7.00−7.08 (m, 12H), 7.39−7.47 (m, 12H), 7.97 (s, 4H), 8.01 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.7, 53.5, 122.3, 123.5, 124.1, 124.8, 126.1, 126.5, 141.9, 142.5, 143.1, 143.3, 146.2, 149.4, 179.6. MALDI-TOF MS: *m*/*z* 1018.3 $[M + H]^+$. Anal. Calcd for $C_{74}H_{40}N_4O_2 \cdot H_2O$: C, 85.86; H, 4.09; N, 5.41. Found: C, 86.12; H, 4.31; N, 5.29.

18: starting from **4** (100 mg, 0.17 mmol) and **8** (49 mg, 0.17 mmol). Yield: 58% (81 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 6H), 5.32 (s, 2H), 5.51 (s, 4H), 5.61 (s, 4H), 6.85−6.87 (m, 2H), 6.92−6.95 (m, 2H), 7.01−7.08 (m, 6H), 7.22−7.29 (m, 4H), 7.35−7.38 (m, 2H), 7.43−7.47 (m, 4H), 7.96 (s, 2H), 8.01 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 48.2, 48.9, 53.5, 122.2, 122.7, 123.9, 124.2, 124.4, 125.4, 126.1, 126.2, 126.4, 134.3, 137.3, 138.8, 142.2, 142.5, 143.3, 143.4, 144.0, 144.2, 144.7, 146.0, 168.6. MALDI-TOF MS: *m*/*z* 825.4 $[M + H]^+$. Anal. Calcd for $C_{58}H_{36}N_2O_4 \cdot H_2O$: C, 82.64; H, 4.54; N, 3.32. Found: C, 82.34; H, 4.51; N, 3.61.

19: starting from **5** (100 mg, 0.16 mmol) and **8** (47 mg, 0.16 mmol). Yield: 64% (90 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 6H), 3.89−3.92 (m, 4H), 4.03−4.13 (m, 4H), 5.60 (s, 2H), 5.78 (s, 2H), 5.98 (s, 2H), 6.82−6.89 (m, 2H), 6.89−6.96 (m, 2H), 6.98−7.03 (m, 2H), 7.03−7.12 (m, 4H), 7.26−7.37 (m, 4H), 7.38−7.51(m, 6H), 7.94−8.05(m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.5, 48.1, 53.6, 59.5, 71.9, 75.2, 122.2, 123.6, 123.7, 124.1, 124.2, 125.2, 126.0, 126.1, 134.7, 137.4, 143.4, 143.5, 145.2, 145.3, 145.9, 146.2. MALDI-TOF MS: *m*/*z* 858.5 $[M]^+$. Anal. Calcd for $C_{60}H_{46}N_2O_4 \cdot 0.5H_2O$: C, 83.02; H, 5.46; N, 3.23. Found: C, 83.04; H, 5.12; N, 3.21.

20: starting from **6** (80 mg, 0.16 mmol) and **7** (47 mg, 0.16 mmol). Yield: 62% (73 mg). Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.62 (s, 2H), 5.77 (s, 2H), 5.93 (s, 2H), 6.90−6.92 (m, 2H), 6.96−6.99 (m, 2H), 7.05−7.09 (m, 6H), 7.32−7.38 (m, 4H), 7.43−7.48 (m, 6H), 8.02 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.6, 47.4, 53.5, 122.2, 124.1, 124.3, 124.8, 125.5, 126.2, 126.5, 141.8, 143.2, 143.5, 143.6, 149.0, 151.3, 179.7. MALDI-TOF MS: *m*/*z* 740.4 $[M + 2H]^+$. Anal. Calcd for $C_{74}H_{40}N_4O_2 \cdot 1.5H_2O$: C, 84.69; H, 4.34; N, 3.66. Found: C, 84.75; H, 4.28; N, 3.54.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for new compounds; determination of the association constant of **15**@C_{60}; X-ray crystallographic file (CIF) for **10**. This material is available free of charge via the Internet at http://pubs.acs.org.